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International Application. No.  
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Title of Invention: **KERATINOUS FIBRE OXIDATION DYEING COMPOSITION CONTAINING A LACCASE AND DYEING METHOD USING SAME**

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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

**Items 11. to 16. below concern other document(s) or information included:**

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:
  - a. ☐ Verified Small Entity Statement.
  - b. ☐ Copy of Notification of Missing Requirements.
  - c. ☒ Verification of Translation

09/600134

PCT/FR98/02830

534 Rec'd PCT/PT 05725-0654

12 JUL 2000  
CALCULATIONS

17. [X] The following fees are submitted:

**Basic National Fee (37 CFR 1.492(a)(1)-(5)):**

Search Report has been prepared by the EPO or JPO.....\$840.00  
 International preliminary examination fee paid to  
 USPTO (37 CFR 1.482).....\$670.00  
 No international preliminary examination fee paid to  
 USPTO (37 CFR 1.482) but international search fee  
 paid to USPTO (37 CFR 1.445(a)(2)).....\$690.00  
 Neither international preliminary examination fee  
 (37 CFR 1.482) nor international search fee  
 (37 CFR 1.445(a)(2)) paid to USPTO.....\$970.00  
 International preliminary examination fee paid to USPTO  
 (37 CFR 1.482) and all claims satisfied provisions  
 of PCT Article 33(1)-(4).....\$ 96.00

**ENTER APPROPRIATE BASIC FEE AMOUNT = \$840.00**

Surcharge of \$130.00 for furnishing the oath or declaration later than  
 [ ] 20 [ ] 30 months from the earliest claimed priority date  
 (37 CFR 1.492(e)).

Claims	Number Filed	Number Extra	Rate	
Total Claims	29-20=	9	X \$18.00	\$162.00
Independent Claims	1- 3=		X \$78.00	\$
Multiple dependent claim(s) (if applicable)			+\$260.00	\$260.00

**TOTAL OF ABOVE CALCULATIONS = \$1262.00**

Reduction by 1/2 for filing by small entity, if applicable. Verified  
 Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28)

**SUBTOTAL = \$1262.00**

Processing fee of \$130.00 for furnishing the English translation later  
 than [ ] 20 [ ] 30 months from the earliest claimed priority date  
 (37 CFR 1.492(f)).

**TOTAL NATIONAL FEE = \$1262.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The  
 assignment must be accompanied by an appropriate cover sheet  
 (37 CFR 3.28, 3.31).

\$40.00 per property + \$  
**TOTAL FEES ENCLOSED = \$1262.00**

Amount to be  
 refunded \$  
 charged \$


[X] A check in the amount of **\$ 1262.00** to cover the above fees is enclosed.  
 [ ] Please charge my Deposit Account No. \_\_\_\_\_ in the amount of  
 \$ \_\_\_\_\_

to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees  
 which may be required, or credit any overpayment to Deposit Account  
 No. 06-0916. A duplicate copy of this sheet is enclosed.

The Commissioner is hereby authorized to charge any other fees due under 37 C.F.R. §1.16  
 or §1.17 during the pendency of this application to our Deposit Account No. 06-0916.

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Submitted: July 12, 2000

COMPOSITION FOR THE OXIDATION DYEING OF KERATINOUS  
FIBERS CONTAINING A LACCASE AND DYEING METHOD USING  
THIS COMPOSITION

The subject of the invention is a composition  
5 for the oxidation dyeing of keratinous fibers and in  
particular human keratinous fibers such as hair,  
comprising, in a medium appropriate for dyeing, 3-  
methyl-4-aminophenol as oxidation base and at least one  
enzyme of laccase type, and the dyeing method using  
10 this composition.

It is known to dye keratinous fibers, and in  
particular human hair, with dyeing compositions  
containing precursors for oxidation dyeing, in  
particular ortho- and para-phenylenediamines, ortho- or  
15 para-aminophenols, heterocyclic bases generally called  
oxidation bases. The precursors for oxidation dyeing  
(oxidation bases) are colorless or weakly colored  
compounds which, combined with oxidizing products, can  
give rise to dye and colored compounds by a process of --  
20 oxidative condensation.

It is also known that the shades obtained  
with these oxidation bases can be varied by combining  
them with couplers or color modifiers, the latter being  
chosen in particular from aromatic meta-diamines, meta-  
25 aminophenols, meta-diphenols and certain heterocyclic  
compounds.

The variety of molecules used in oxidation bases and couplers allows a rich palette of colors to be obtained.

The so-called "permanent" color obtained by means of these oxidation dyes should moreover satisfy a number of requirements. Thus, it should have no drawbacks from the toxicological point of view, it should make it possible to obtain shades of the desired intensity and it should exhibit good resistance toward external agents (light, adverse weather conditions, washing, permanent waving, perspiration, rubbing).

The dyes should also make it possible to cover gray hair, and thus should be the least selective possible, that is to say they should make it possible to obtain the smallest possible differences in color all along the same keratinous fiber, which may indeed be differently sensitized (i.e. damaged) between its tip and its root.

The oxidation dyeing of keratinous fibers is generally carried out in an alkaline medium, in the presence of hydrogen peroxide. However, the use of alkaline media in the presence of hydrogen peroxide has the disadvantage of causing substantial degradation of the fibers, as well as decoloring of the keratinous fibers which is not always desirable.

The oxidation dyeing of keratinous fibers can also be carried out with the aid of oxidizing systems different from hydrogen peroxide such as enzymatic

systems. Thus, it has already been proposed in Patent  
US 3,251,742, Patent Applications FR-A-2,112,549,  
FR-A-2,694,018, EP-A-0,504,005, WO95/07988, WO95/33836,  
WO95/33837, WO96/00290, WO97/19998 and WO97/19999 to  
5 dye keratinous fibers with compositions comprising at  
least [lacuna] oxidation dye, or at least one melanin  
precursor, in combination with enzymes of the laccase  
type, said compositions being brought into contact with  
atmospheric oxygen. These dyeing formulations, although  
10 used under conditions which do not cause degradation of  
the keratinous fibers comparable to that caused by  
dyeings carried out in the presence of hydrogen  
peroxide, lead to colors which are still inadequate  
both from the point of view of homogeneity of the color  
15 distributed along the fiber (unison), from the point of  
view of chromaticity (luminosity) and of the dyeing  
power.

In point of fact, the Applicant Company has  
now just discovered that it is possible to obtain novel  
20 dyes, which are capable of resulting in powerful  
colorings without causing significant degradation of  
the keratinous fibers, which exhibit low selectivity  
and which exhibit good resistance to various attacks to  
which the fibers may be subjected, by combining 3-  
25 methyl-4-aminophenol, as oxidation base, and at least  
one enzyme of laccase type.

This discovery forms the basis of the present  
invention.

The first subject of the invention is therefore a ready-to-use composition for the oxidation dyeing of keratinous fibers and in particular human keratinous fibers such as hair, which comprises, in a medium appropriate for dyeing:

- 3-methyl-4-aminophenol and/or at least one of its addition salts with an acid, as oxidation base, and
- at least one enzyme of laccase type.

The ready-to-use dyeing composition in accordance with the invention results in powerful colorings which exhibit low selectivity and excellent properties of resistance both with respect to atmospheric agents, such as light and bad weather, and with respect to perspiration and various treatments to which the hair may be subjected (washing, permanent deformation).

The subject of the invention is also a method for the oxidation dyeing of keratinous fibers using this ready-to-use dyeing composition.

3-Methyl-4-aminophenol and/or its addition salt(s) with an acid preferably represent from 0.0005 to 12% approximately of the total weight of the dyeing composition in accordance with the invention and still more preferably from 0.005 to 6% by weight approximately of this weight.

The laccase(s) used in the ready-to-use dye composition in accordance with the invention may be chosen in particular from laccases of plant origin,

animal origin, fungal origin (yeasts, molds, fungi) or bacterial origin, organisms which may be of mono- or pluricellular origin. The laccase(s) used in the ready-to-use dyeing composition in accordance with the invention can also be obtained by biotechnology.

Among the laccases of plant origin which can be used according to the invention, there may be mentioned the laccases produced by plants which perform chlorophyll synthesis such as those indicated in Patent Application FR-A-2,694,018.

There may be mentioned, in particular, the laccases present in the extracts of Anacardiaceae such as for example the extracts of *Magnifera indica*, *Schinus molle* or *Pleiogynium timoriense*, in the extracts of Podocarpaceae, *Rosmarinus off.*, *Solanum tuberosum*, *Iris sp.*, *Coffea sp.*, *Daucus carota*, *Vinca minor*, *Persea americana*, *Catharethus roseus*, *Musa sp.*, *Malus pumila*, *Ginkgo biloba*, *Monotropa hypopithys* (Indian pipe), *Aesculus sp.*, *Acer pseudoplatanus*, *Prunus persica* and *Pistacia palaestina*.

Among the laccases of fungal origin optionally obtained by biotechnology which can be used according to the invention, there may be mentioned the laccase(s) derived from *Polyporus versicolor*, *Rhizoctonia praticola* and *Rhus vernicifera* such as described, for example, in Patent Applications FR-A-2,112,549 and EP-A-504005, the laccases described in Patent Applications WO95/07988, WO95/33836,

WO95/33837, WO96/00290, WO97/19998 and WO97/19999,  
 whose content is an integral part of the present  
 description, such as for example the laccase(s) derived  
 from *Scytalidium*, *Polyporus pinsitus*, *Myceliophthora*  
 5 *thermophila*, *Rhizoctonia solani*, *Pyricularia orizae*, or  
 variants thereof. There may also be mentioned the  
 laccase(s) derived from *Trametes versicolor*, *Fomes*  
*fomentarius*, *Chaetomium thermophile*, *Neurospora crassa*,  
*Coriolus versicol*, *Botrytis cinerea*, *Rigidoporus*  
 10 *lignosus*, *Phellinus noxius*, *Pleurotus ostreatus*,  
*Aspergillus nidulans*, *Podospora anserina*, *Agaricus*  
*bisporus*, *Ganoderma lucidum*, *Glomerella cingulata*,  
*Lactarius piperatus*, *Russula delica*, *Heterobasidion*  
*annosum*, *Thelephora terrestris*, *Cladosporium*  
 15 *cladosporioides*, *Cerrena unicolor*, *Coriolus hirsutus*,  
*Ceriporiopsis subvermispora*, *Coprinus cinereus*,  
*Panaeolus papilionaceus*, *Panaeolus sphinctrinus*,  
*Schizophyllum commune*, *Dichomitius squalens* and  
 variants thereof.

20           The laccases of fungal origin optionally  
 obtained by biotechnology will be preferably chosen.

          The enzymatic activity of the laccases used  
 in accordance with the invention and which have  
 syringaldazine among their substrates can be defined  
 25 from the oxidation of syringaldazine under aerobic  
 conditions. The Lacu unit corresponds to the quantity  
 of enzyme catalyzing the conversion of 1 mmol of  
 syringaldazine per minute at a pH of 5.5 and at a



temperature of 30°C. The unit U corresponds to the quantity of enzyme producing a delta absorbance of 0.001 per minute, at a wavelength of 530 nm, using syringaldazine as substrate, at 30°C and at a pH of 5. The enzymatic activity of the laccases of the invention can also be defined from the oxidation of para-phenylenediamine. The ulac unit corresponds to the quantity of enzyme producing a delta absorbance of 0.001 per minute, at a wavelength of 496.5 nm, using para-phenylenediamine as substrate (64 mM) at 30°C and at a pH of 5.

According to the invention, it is preferable to determine the enzymatic activity in ulac units.

According to a preferred embodiment, the dyeing composition in accordance with the invention also contains one or more couplers, so as to modify or to enrich with highlights the shades obtained by using 3-methyl-4-aminophenol.

The couplers which can be used in the dyeing composition in accordance with the invention can be chosen from the couplers conventionally used in oxidation dyeing and among which may in particular be mentioned meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers.

These couplers are chosen more particularly from 2-methyl-5-aminophenol, 5-N-( $\beta$ -hydroxyethyl)amino-2-methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxy-

benzene, 2,4-diamino-1-( $\beta$ -hydroxyethyloxy)benzene,  
 2-amino-4-N-( $\beta$ -hydroxyethyl)amino-1-methoxybenzene,  
 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane,  
 sesamol,  $\alpha$ -naphthol, 6-hydroxyindole, 4-hydroxyindole,  
 5 4-hydroxy-N-methylindole, 6-hydroxyindoline,  
 2,6-dihydroxy-4-methylpyridine, 1-H-3-methylpyrazole-5-  
 one, 1-phenyl-3-methylpyrazole-5-one, 2,6-dimethyl-  
 pyrazolo[1,5-b]-1,2,4-triazole, 2,6-dimethyl[3,2-c]-  
 1,2,4-triazole, 6-methylpyrazolo[1,5-a]benzimidazole,  
 10 and their addition salts with an acid.

When they are present, the coupler(s)  
 preferably represent from 0.0001 to 8% by weight  
 approximately of the total weight of the dyeing  
 composition, and still more preferably from 0.005 to 5%  
 15 by weight approximately of this weight.

The dyeing composition in accordance with the  
 invention can also contain, in addition to the 3-  
 methyl-4-aminophenol and/or its addition salts with an  
 acid, at least one additional oxidation base which can --  
 20 be chosen from oxidation bases conventionally used for  
 oxidation dyeing. They can be chosen in particular from  
 para-phenylenediamines, double bases, para-  
 aminophenols, ortho-aminophenols and heterocyclic  
 oxidation bases.

25 Among the para-phenylenediamines, there may  
 be mentioned more particularly by way of example para-  
 phenylenediamine, para-tolylenediamine, 2-chloro-para-  
 phenylenediamine, 2,3-dimethyl-para-phenylenediamine,

2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine,  
 5 4-amino-N,N-diethyl-3-methylaniline, N,N-bis( $\beta$ -hydroxyethyl)-para-phenylenediamine, 4-N,N-bis( $\beta$ -hydroxyethyl)amino-2-methylaniline, 4-N,N-bis( $\beta$ -hydroxyethyl)amino-2-chloroaniline, 2- $\beta$ -hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine,  
 10 2-isopropyl-para-phenylenediamine, N-( $\beta$ -hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl- $\beta$ -hydroxyethyl)-para-phenylenediamine, N-( $\beta$ , $\gamma$ -dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-para-phenylenediamine, 2- $\beta$ -acetylaminoethyloxy-para-phenylenediamine, N-( $\beta$ -methoxyethyl)-para-phenylenediamine, and their addition salts with an  
 15 acid.

Among the para-phenylenediamines mentioned hereinabove, there are most particularly preferred para-phenylenediamine, para-tolylenediamine, 2-isopropyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis( $\beta$ -hydroxyethyl)-para-

phenylenediamine, 2-chloro-para-phenylenediamine, 2- $\beta$ -acetylaminooethyloxy-para-phenylenediamine, and their addition salts with an acid.

Among the bisphenylalkylenediamines, there  
 5 may be mentioned more particularly by way of example  
 N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-  
 diaminopropanol, N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-  
 aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)-  
 tetramethylenediamine, N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-  
 10 bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-  
 methylaminophenyl)tetramethylenediamine, N,N'-  
 bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylene-  
 diamine, 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane,  
 and their addition salts with an acid.

15 Among the para-aminophenols, there may be  
 mentioned more particularly by way of example para-  
 aminophenol, 4-amino-3-fluorophenol, 4-amino-3-  
 hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-  
 hydroxymethylphenol, 4-amino-2-methoxymethylphenol,  
 20 4-amino-2-aminomethylphenol, 4-amino-2-( $\beta$ -  
 hydroxyethylaminomethyl)phenol, 4-amino-2-fluorophenol,  
 and their addition salts with an acid.

Among the ortho-aminophenols, there may be  
 mentioned more particularly by way of example  
 25 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-  
 methylphenol, 5-acetamido-2-aminophenol, and their  
 addition salts with an acid.

Among the heterocyclic bases, there may be mentioned more particularly by way of example pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

5           When they are used, the additional oxidation base(s) preferably represent from 0.0005 to 12% by weight approximately of the total weight of the dyeing composition in accordance with the invention and still more preferably from 0.005 to 6% by weight

10 approximately of this weight.

In general, the addition salts with an acid which can be used in the context of the dyeing compositions of the invention (oxidation bases and couplers) are in particular chosen from hydrochlorides, 15 hydrobromides, sulfates and tartrates, lactates and acetates.

The dyeing composition in accordance with the invention may also contain one or more direct dyes.

The medium appropriate for dyeing (or 20 carrier) of the ready-to-use dyeing composition in accordance with the invention generally consists of water or of a mixture of water and of at least one organic solvent in order to solubilize the compounds which might not be sufficiently soluble in water.

25           The pH of the ready-to-use composition in accordance with the invention is chosen such that the enzymatic activity of the laccase is sufficient. It is generally of between 4 and 11 approximately, and

preferably between 6 and 9 approximately. It can be adjusted to the desired value by means of acidifying or basifying agents commonly used in dyeing keratinous fibers.

5           The ready-to-use dyeing composition in accordance with the invention may also contain various adjuvants conventionally used in compositions for dyeing hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures  
10 thereof, polymers, antioxidants, enzymes different from the laccases used in accordance with the invention, such as for example peroxidases or oxidoreductases containing 2 electrons, penetrating agents, sequestering agents, perfumes, buffers, dispersing  
15 agents, thickeners, film-forming agents, preservatives, opacifying agents or vitamins.

Of course, persons skilled in the art will be careful to choose this or these optional additional compounds such that the advantageous properties  
20 intrinsically attached to the ready-to-use dyeing composition in accordance with the invention are not, or substantially not, impaired by the addition(s) envisaged.

The ready-to-use dyeing composition in  
25 accordance with the invention can be provided in various forms, such as in the form of liquids, creams, gels, optionally pressurized, or in any other form appropriate for dyeing keratinous fibers, in particular

human hair. In this case, the 3-methyl-4-aminophenol and, if appropriate, the additional oxidation dyes and the enzyme(s) of laccase type are present in the same ready-to-use composition, and consequently said

5 composition should be free of gaseous oxygen, so as to avoid any premature oxidation of the oxidation dye(s).

The subject of the invention is also a method of dyeing keratinous fibers, and in particular human keratinous fibers such as hair, using the ready-to-use  
10 dyeing composition as defined above.

According to this method, at least one ready-to-use dyeing composition as defined above is applied to the fibers for a sufficient time to develop the desired color, after which they are rinsed, optionally  
15 washed with shampoo, rinsed again and dried.

The time necessary for the development of the color on the keratinous fibers is generally between 3 and 60 minutes and still more precisely 5 and 40 minutes.

20 According to one particular embodiment of the invention, the method comprises a preliminary step consisting in storing in a separate form, on the one hand, a composition (A) comprising, in a medium appropriate for dyeing, 3-methyl-4-aminophenol and/or  
25 at least one of its addition salts with an acid and, on the other hand, a composition (B) containing, in a medium appropriate for dyeing, at least one enzyme of laccase type, and then in mixing them at the time of

use before applying this mixture to the keratinous fibers.

Another subject of the invention is a multi-compartment device or dyeing (kit) or any other multi-compartment packaging system in which a first compartment contains the composition (A) as defined above and a second compartment contains a composition (B) as defined above. These devices may be equipped with a means which makes it possible to deliver the desired mixture to the hair, such as the devices described in Patent FR-2,586,913 in the name of the applicant.

The following examples are intended to illustrate the invention without, however, limiting the scope thereof.

#### DYEING EXAMPLE

The following dyeing composition was prepared:

- |    |  |        |    |
|----|--|--------|----|
| -  | 3-Methyl-4-aminophenol   | 0.25 g | -- |
| 20 | - 5-N-( $\beta$ -Hydroxyethyl)amino-2-methylphenol               | 0.30 g |    |
| -  | Laccase obtained from <i>Rhus vernicifera</i>                    |        |    |
|    | containing 180 units/mg sold by the                              |        |    |
|    | company ICN  | 1.8 g  |    |
| -  | (C <sub>8</sub> -C <sub>10</sub> )Alkyl polyglucoside in aqueous |        |    |
| 25 | solution containing 60% of active substance                      |        |    |
|    | (A.S.), sold under the name                                      |        |    |
|    | ORAMIX CG110® by the company SEPPIC                              | 8.0 g  |    |
| -  | Ethanol  | 20 g   |    |



- |                       |                |        |
|-----------------------|----------------|--------|
| - pH agent            | q.s.           | pH 6.5 |
| - Demineralized water | q.s. for 100 g |        |

The ready-to-use dyeing composition described above was applied to locks of natural gray hair which is 90% white for 40 minutes at a temperature of 30°C. The hair was then rinsed and then dried.

The hair was dyed in a coppery gold shade.

In the dyeing composition described above, the *Rhus vernicifera* laccase at 180 units/mg, sold by the company Sigma, can be replaced by 1.0 g of *Pyricularia orizae* laccase at 100 units/mg sold by the company ICN.

## CLAIMS

1. A ready-to-use composition for the oxidation dyeing of keratinous fibers and in particular human keratinous fibers such as hair, which comprises,  
5 in a medium appropriate for dyeing:  
- 3-methyl-4-aminophenol and/or at least one of the [sic] its addition salts with an acid, as oxidation base, and  
- at least one enzyme of laccase type.
- 10 2. The composition as claimed in claim 1, wherein the 3-methyl-4-aminophenol and/or its addition salt(s) with an acid represent from 0.0005 to 12% by weight of the total weight of the dyeing composition.
- 15 3. The composition as claimed in claim 2, wherein the 3-methyl-4-aminophenol and/or its addition salt(s) with an acid represent from 0.005 to 6% by weight of the total weight of the dyeing composition.
- 20 4. The composition as claimed in any one of claims 1 to 3, wherein the laccase is chosen from laccases of plant origin, animal origin, fungal origin or bacterial origin and from laccases obtained by biotechnology.
- 25 5. The composition as claimed in claim 4, wherein the laccase is of plant origin and is chosen from the laccases present in the extracts of Anacardiaceae, Podocarpaceae, Rosmarinus off., Solanum tuberosum, Iris sp., Coffea sp., Daucus carota, Vinca

minor, *Persea americana*, *Catharethus roseus*, *Musa* sp.,  
*Malus pumila*, *Ginkgo biloba*, *Monotropa hypopithys*  
 (Indian pipe), *Aesculus* sp., *Acer pseudoplatanus*,  
*Prunus persica* and *Pistacia palaestina*.

5           6. The composition as claimed in claim 4,  
 wherein the laccase is of microbial origin or is  
 obtained by biotechnology.

7. The composition as claimed in claim 6,  
 wherein the laccase is chosen from the laccases derived  
 10 from *Polyporus versicolor*, *Rhizoctonia praticola*, *Rhus*  
*verniciifera*, *Scytalidium*, *Polyporus pinsitus*,  
*Myceliophthora thermophila*, *Rhizoctonia solani*,  
*Pyricularia orizae*, *Trametes versicolor*, *Fomes*  
*fomentarius*, *Chaetomium thermophile*, *Neurospora crassa*,  
 15 *Coriolus versicol*, *Botrytis cinerea*, *Rigidoporus*  
*lignosus*, *Phellinus noxius*, *Pleurotus ostreatus*,  
*Aspergillus nidulans*, *Podospora anserina*, *Agaricus*  
*bisporus*, *Ganoderma lucidum*, *Glomerella cingulata*,  
*Lactarius piperatus*, *Russula delica*, *Heterobasidion*  
 20 *annosum*, *Thelephora terrestris*, *Cladosporium*  
*cladosporioides*, *Cerrena unicolor*, *Coriolus hirsutus*,  
*Ceriporiopsis subvermispora*, *Coprinus cinereus*,  
*Panaeolus papilionaceus*, *Panaeolus sphinctrinus*,  
*Schizophyllum commune*, *Dichomitius squalens* and  
 25 variants thereof.

8. The composition as claimed in any one of  
 the preceding claims, wherein the quantity of

laccase(s) is between 0.5 and 200 Lacu per 100 g of dyeing composition.

9. The composition as claimed in any one of the preceding claims, which contains one or more  
5 couplers chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers.

10. The composition as claimed in claim 9, wherein the couplers are chosen from 2-methyl-5-aminophenol, 5-N-( $\beta$ -hydroxyethyl)amino-2-methylphenol,  
10 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-( $\beta$ -hydroxyethyloxy)benzene, 2-amino-4-N-( $\beta$ -hydroxyethyl)amino-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane,  
15 sesamol,  $\alpha$ -naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1-H-3-methylpyrazole-5-one, 1-phenyl-3-methylpyrazole-5-one, 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole, 2,6-dimethyl[3,2-c]-  
20 1,2,4-triazole, 6-methylpyrazolo[1,5-a]benzimidazole, and their addition salts with an acid.

11. The composition as claimed in claim 9 or 10, wherein the coupler(s) represent from 0.0001 to 8% by weight of the total weight of the dyeing  
25 composition.

12. The composition as claimed in claim 11, wherein the coupler(s) represent from 0.005 to 5% by weight of the total weight of the dyeing composition.

13. The composition as claimed in any one of the preceding claims, which contains at least one additional oxidation base chosen from para-phenylenediamines, double bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

14. The composition as claimed in claim 13, wherein the additional oxidation base(s) represent from 0.0005 to 12% by weight of the total weight of the dyeing composition.

15. The composition as claimed in claim 14, wherein the additional oxidation base(s) represent from 0.005 to 6% by weight of the total weight of the dyeing composition.

16. The composition as claimed in any one of the preceding claims, wherein the addition salts with an acid are chosen from hydrochlorides, hydrobromides, sulfates and tartrates, lactates and acetates.

17. The composition as claimed in any one of the preceding claims, wherein the medium appropriate for dyeing consists of water or of a mixture of water and at least one organic solvent.

18. The composition as claimed in any one of the preceding claims, which has a pH of [lacuna] 4 and 11.

19. A method of dyeing keratinous fibers, and in particular human keratinous fibers such as hair, which comprises the application of at least one ready-to-use dyeing composition as defined in any one of the

preceding claims to said fibers for a sufficient time to develop the desired color.

20. The method as claimed in claim 19, which comprises a preliminary step consisting in storing in a  
5 separate form, on the one hand, a composition (A) comprising, in a medium appropriate for dyeing, 3-methyl-4-aminophenol and/or at least one of its addition salts with an acid, as oxidation base, and, on the other hand, a composition (B) containing, in a  
10 medium appropriate for dyeing, at least one laccase enzyme, and then in mixing them at the time of use before applying this mixture to the keratinous fibers.

21. A multicompartment device or dyeing "kit", which comprises a first compartment containing  
15 the composition (A) as defined in claim 20 and a second compartment containing the composition (B) as defined in claim 20.

# Declaration and Power of Attorney for Patent Application

## Déclaration et Pouvoir pour Demand de Brevet

### French Language Declaration

En tant que l'inventeur nommé ci-après, je déclare par le présent acte que:

Mon domicile, mon adresse postale et ma nationalité sont ceux figurant ci-dessous à côté de mon nom.

Je crois être le premier inventeur original et unique (si un seul nom est mentionné ci-dessous), ou l'un des premiers co-inventeurs originaux (si plusieurs noms sont mentionnés ci-dessous) de l'objet revendiqué, pour lequel une demande de brevet a été déposée concernant l'invention intitulée

et dont la description est fournie ci-joint à moins que la case suivante n'ait été cochée:

☒ a été déposée le \_\_\_\_\_  
sous le numéro de demande des Etats-Unis ou le  
numéro de demande international PCT  
\_\_\_\_\_ et modifiée  
\_\_\_\_\_ (les cas échéant).

Je déclare par le présent acte avoir passé en revue et compris le contenu de la description ci-dessus, revendications comprises, telles que modifiées par toute modification dont il aura été fait référence ci-dessus.

Je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations.

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

KERATINOUS FIBRE OXIDATION DYEING  
COMPOSITION CONTAINING A LACCASE AND  
DYEING METHOD USING SAME

the specification of which is attached hereto unless the following box is checked:

☒ was filed on December 22, 1998 as United States Application Number or PCT International Application Number PCT/FR98/02830 and was amended on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

## French Language Declaration

Je revendique par le présent acte avoir la priorité étrangère, en vertu du Titre 35, § 119(a)-(d) ou § 365(b) du Code des Etats-Unis, sur toute demande étrangère de brevet ou certificat d'inventeur ou, en vertu du Titre 35, § 365(a) du même Code, sur toute demande internationale PCT désignant au moins un pays autre que les Etats-Unis et figurant ci-dessous et, en cochant la case, j'ai aussi indiqué ci-dessous toute demande étrangère de brevet, tout certificat d'inventeur ou toute demande internationale PCT ayant une date de dépôt précédant celle de la demande à propos de laquelle une priorité est revendiquée.

Prior foreign application(s)  
Demande(s) de brevet antérieure(s)

98/00,260	France
(Number)	(Country)
(Numéro)	(Pays)
(Number)	(Country)
(Numéro)	(Pays)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 119(e) du Code des Etats-Unis, de toute demande de brevet provisoire effectuée aux Etats-Unis et figurant ci-dessous.

(Application No.)	(Filing Date)
(N° de demande)	(Date de dépôt)
(Application No.)	(Filing Date)
(N° de demande)	(Date de dépôt)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 120 du Code des Etats-Unis, de toute demande de brevet effectuée aux Etats-Unis, ou en vertu du Titre 35, § 365(c) du même Code, de toute demande internationale PCT désignant les Etats-Unis et figurant ci-dessous et, dans la mesure où l'objet de chacune des revendications de cette demande de brevet n'est pas divulgué dans la demande antérieure américaine ou internationale PCT, en vertu des dispositions du premier paragraphe du Titre 35, § 112 du Code des Etats-Unis, je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations, dont laquelle est devenue disponible entre la date de dépôt de la demande antérieure, et la date de dépôt de la demande nationale ou internationale PCT de la présente demande:

(Application No.)	(Filing Date)
(N° de demande)	(Date de dépôt)
(Application No.)	(Filing Date)
(N° de demande)	(Date de dépôt)

Je déclare par le présent acte que toute déclaration ci-incluse est, à ma connaissance, véridique et que toute déclaration formulée à partir de renseignements ou de suppositions est tenue pour véridique; et de plus, que toutes ces déclarations ont été formulées en sachant que toute fausse déclaration volontaire ou son équivalent est passible d'une amende ou d'une incarcération, ou des deux, en vertu de la Section 1001 du Titre 18 du Code des Etats-Unis, et que de telles déclarations volontairement fausses risquent de compromettre la validité de la demande de brevet ou du brevet délivré à partir de celle-ci.

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International Application which designated at least one country other than the United States, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Not Claimed  
Droit de priorité non revendiqué

13 January 1998	<input type="checkbox"/>
(Day/Month/Year Filed)	
(Jour/Mois/Anné de dépôt)	
(Day/Month/Year Filed)	<input type="checkbox"/>
(Jour/Mois/Anné de dépôt)	

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International Application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose any or all information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Status) (patented, pending, abandoned)
(Status) (breveté, en cours d'examen, abandonné)
(Status) (patented, pending, abandoned)
(Status) (breveté, en cours d'examen, abandonné)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.



## French Language Declaration

POUVOIRS: En tant que l'inventeur cité, je désigne par la présente l'(les) avocat(s) et/ou agent(s) suivant(s) pour qu'ils poursuive(nt) la procédure de cette demande de brevet et traite(nt) toute affaire s'y rapportant avec L'Office des brevets et des marques: (mentionner le nom et le numéro d'enregistrement).

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this patent application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number):

30  
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